AD-A266 759 NTATION PAGE

Form Approved
OMB No. 0704-0188

...ated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	May 28, 1993	Final Report- phase I- 8/1/92-3/1/93

4. TITLE AND SUBTITLE

Single Crystal Diamond Films

5. FUNDING NUMBERS

DAAL03-92-C-0030

6. AUTHOR(S)

Dr. Stephen N. Bunker

Mr. Richard Sahagian

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Implant Sciences Corporation
107 Audubon Rd.
#5 Corporate Place
Wakefield, MA 01880-1246

DTIC ELECTE JUL 12 1993 S E D

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211
ATTN: Mr. Richard Ulsh

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

ARO 30461.1-MS-SBI

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

Diamond films are important for radiation tolerant devices. However, fabrication of single crystal films has proven to be much more difficult than polycrystalline deposits. A novel deposition process is proposed which can be used to deposit diamond on a seed crystal. The technique permits patterned deposits in islands and offers the potential of a new method for attempting to dope diamond semiconductors.

14. SUBJECT TERMS

Single Crystal, Diamond, Thin Films, Radiation Tolerant

15. NUMBER OF PAGES

27

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

FINAL REPORT FOR
SINGLE CRYSTAL DIAMOND FILMS

CONTRACT # DAAL 03-92-C-0030

Accesion For	
NTIS CRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution /	
Availability Codes	

Dist	Avail and / or Special
A-1	

Submitted to:
Mr. Richard Ulsh
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

Submitted by:
IMPLANT SCIENCES CORPORATION
107 Audubon Rd.
#5 Corporate Place
Wakefield, MA 01880-1246

93 7 08 152

93-15570

I.   INTRODUCTION

Thin film diamond offers the highest radiation resistance of any semiconductor material. Characteristics such as its wide bandgap and optical properties make it a highly desired electronic material. However the fabrication of a single crystal film has proven to be much more of a challenge than the growth of polycrystalline deposits. Chemical vapor deposition (CVD) techniques have been the most popular for depositing thin film diamond. CVD has two major limitations; First, polycrystalline diamond films are extremely rough, exhibiting multi-faceted surfaces with considerable topography. Second, a reliable method for n-type doping is yet unknown. These characteristics coupled with lack of good crystallinity are not desirable for semiconductor processing.

The process investigated is a novel approach to diamond deposition which combines many of the specialized strengths and characteristics of existing methods for epitaxial growth. The technique utilizes the ion implantation of a thin "solvent" film with carbon. The liquid film is in contact with a substrate which serves as single crystal seed. Figure 1 illustrates the technique. Appropriate solvents must have the ability to dissolve carbon only slightly and not react with the substrate seed. The molten solvent must also be capable of wetting the substrate surface uniformly and not congeal into discrete beads and droplets.

Carbon is implanted into the solvent layer using a modified ion implanter. As the carbon concentration exceeds its solubility limit, atoms precipitate and crystallize according to the lattice of the seed. In choosing the bombardment parameters, the implanted carbon distribution can be placed so as to encourage growth of the film at the solvent-substrate interface.
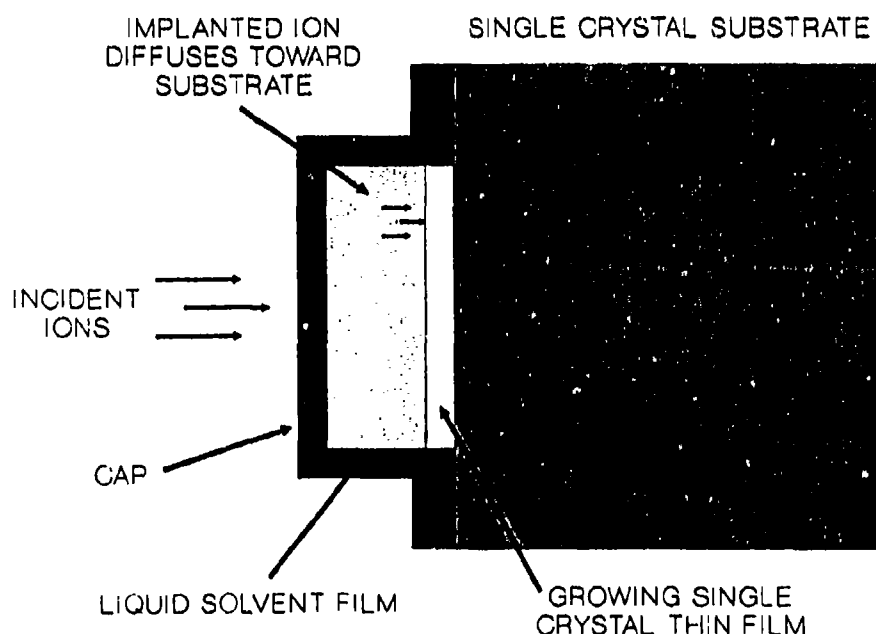

Figure 1.Implantation Geometry of the Solvent-Coated Substrate With the Various Layers

1

1.1 TECHNICAL APPROACH

The investigated technique is simple in principle and thus quite versatile. A wide variety of semiconductors, including difficult systems such as ternary compounds and refractories, can be fabricated. There are two basic versions of this technique. First, in the reaction version a thin liquid film of solvent is deposited onto a single crystal substrate which will act as a seed. The liquid solvent and implanted ion react to form a compound in situ to form the semiconductor, which then deposits on the seed as a single crystal. An example would be arsenic implanted into solvent gallium to make GaAs. In the second version the implanted ion is inert in the liquid, and in this case the solvent must not react with or significantly dissolve the implanted species. The optimal liquid solvent will also melt at a temperature near a suitable deposition temperature for crystal growth. The solvent is also required to fully wet the substrate without agglomerating or "balling up" into discrete droplets.

A mass analyzed ion beam of carbon is directed at the sample at a zero degree incidence angle. The solvent thickness and ion energy are selected to optimize growth rate. The carbon ions must come to rest <u>inside</u> the solvent coating. The location of the deposited carbon is critical. Should the peak of the distribution come to rest too close to the solvent-substrate interface, ions reaching the substrate would damage the single crystal lattice of the seed. As the concentration of the implanted carbon increases to the solubility limit, the liquid becomes saturated. Under these conditions, the carbon will precipitate out to deposit preferentially on either the solvent/substrate or the solvent/vacuum interface, and the relative probability will be determined by the distance to the respective interface. Carbon atoms precipitated at the vacuum/solvent interface will probably be converted to graphite or amorphous carbon because of the continual bombardment through the layer.

Deposits forming on the solvent/vacuum interface are temporary since they are sputtered off by the incoming beam. The carbon depositing at the substrate should form epitxially in much the same manner as for liquid phase epitaxy (LPE). The lattice parameters of the substrate seed and ambient temperature are critical in defining the defect density of the deposited film.

Gallium and indium are good candidates for the liquid thin film. Both materials have low melting points, low vapor pressure, excellent wetting, and low or no solubility of carbon in the liquid state. In traditional liquid phase epitaxy the gallium melt and substrate seed would be separately brought to a temperature just above the liquidus line. Then the two would be physically moved together and allowed to cool to a temperature just below the liquidus line. The gallium (or indium) metal would become supersaturated and carbon would begin to precipitate out. Cooling would continue until much of the carbon is extracted out of solution. However, the new process described in this report can be done at constant temperature, because the precipitating material is constantly being replenished and the solution is always just at the supersaturation level. Additionally, the difficult task of separately heating and then physically merging the substrate and melt is eliminated. Contamination should also be minimized since there is no requirement for a containment vessel for the melt.

2

Another anticipated advantage of the proposed method is the lack of constraint on the substrate during processing other than to have the film remain a liquid which wets the surface. Also, since the growth occurs in the liquid film and not in contact with a container or the ambient vacuum environment, it is possible to grow extremely pure materials. Growth of the deposited layer will occur preferentially at the areas where the liquid film is the thinnest, since precipitation will occur over the shortest path between source and sink. Thus, a mask could be used to deposit the material selectively in different features on the substrate.

Factors such as substrate temperature must be controllable in order to maintain the melt and stabilize the formation of the phase of the material. For example, it was initially thought that to avoid the implanted carbon from coming down as graphite instead of diamond, the substrate temperature should be relatively high. Another potentially important capability of this novel approach is the possibility of doping while depositing the diamond with a second ion beam. Both the diamond and dopant rates of deposition could be controlled using this concept. Melt materials which are inert to both carbon and the dopant are required.

Prior to this research, ion implantation into liquids had never been deliberately attempted, although most likely it had occurred accidentally when implant targets melted due to overheating. In summary the benefits from the successful completion of this research are as follows:

1. Deposition of a single crystal thin film
2. Ultra-high purity deposition
3. Wide selection of semiconductor materials possible
4. Excellent control of growth rate
5. Low temperature process - reduced stress due to thermal mismatch
6. Graded interface allowing for better lattice matching
7. Ability to selectively deposit to make features by use of a mask
8. Ternary compounds possible with use of dual ion beams

1.2 PHASE I RESEARCH OBJECTIVES

The proposed program had limited objectives due to the high risk, high payoff nature of the proposed technique.

The research objectives of the program are as follows;

1. Choose and deposit appropriate thin solvent film.
2. Determine if capping layer is required.
3. Fabricate single crystal diamond by ion implantation epitaxy.
4. Assess the semiconductor potential of the resulting films, and prepare a final report.

2.0   TECHNICAL RESULTS

2.1   MATERIALS SELECTION

The proper selection of materials for the two major components of the system, the thin film solvent and the single crystal substrate seed is crucial. The choice of a capping material is less crucial and for certain combinations may not be required. The requirements of the thin film solvent have been mentioned above and are recapped below;

1.   Must completely wet the substrate surface.
2.   Must be inert to the substrate, carbon, and the cap if required.
3.   Must melt slightly above room temperature.
4.   Must have a high boiling point.
5.   Should have low vapor pressure even at elevated temperatures.

Indium and gallium are two materials which immediately stood out as candidates. Gallium wets most materials and has the broadest temperature range as a liquid for any element. The original list of possible solvent materials which fit one or two of the above criteria are listed in Table 1. Also considered were eutectic mixtures in various combinations of gallium, indium and tin. The field of candidates was quickly reduced due the elimination of those materials which react with silicon.

TABLE 1: Candidate Liquid Thin Film Solvent Material

Gallium	Nickel
Indium	Copper
Tin	Cadmium
Gold	Tellurium
Aluminum	Silver
Boron oxide	Antimony

Potential substrate materials were selected for a close lattice match with diamond. A close, but not exact lattice match is desired to simplify subsequent analysis. Additionally, the purpose of the research was to investigate the problems associated with the growth process and not explore the well-known problems of lattice matching. Table 2 contains a list of possible substrate/seed candidate materials. Library research indicated that Cd, Te, CdTe, Ni and Cu are inappropriate for use with gallium and Cd, Te and CdTe are inappropriate for indium since they will alloy. The research was conducted using silicon substrates (3:2 lattice constant ratio with diamond) for early runs, and eventually silicon carbide and single crystal diamond were used. The silicon carbide substrate was purchased as 6H, the only type commercially available.

4

The diamond was <100>. Silicon was <111>.

Table 2. Candidate Substrate Materials

Silicon
Diamond
Silicon Carbide
Sapphire
Nickel
Copper
3-5 semiconductors

2.2 FABRICATION OF SAMPLES FOR IMPLANTATION

Preparation of silicon substrates

The latent oxide resident on silicon had to be removed prior to the deposition of the solvent layer. A method to etch silicon and cap it with a temporary hydrogen monolayer was described by D.K. Fork et al[1]. A procedure based on that method was developed. The technique terminates the silicon surface with hydrogen making it passive to oxidation. The hydrogen is removed leaving bare silicon by heating over 500°C. The capped substrates can be exposed to air for a short time with no deleterious effects. The technique is performed in a nitrogen filled positive pressure glove box and the samples are transferred to the process chamber in a nitrogen filled vessel. The silicon substrate preparation procedure is given below;

1. Degrease and clean related tools and fixtures.
2. Purge glove box with nitrogen.
3. Under a vented hood and with proper protection, mix hydrofluoric acid, methanol, and distilled water at a 1:10:1 ratio, respectively.
4. Place solution, samples, fixtures and tooling into the glove box. Set up nitrogen feedline to purge transfer vessel.
5. Allow glove box to purge until the volume has been replaced at least ten times.
6. Depending on the oxide thickness (usually 30 Å), etch for an appropriate time. (usually no more than 60 seconds)
7. Check that the oxide is removed by taking it out of the solution and observing the liquid remaining on the sample surface. If the oxide is adequately removed, the solution should slide off in sheets and not ball up in little droplets on the surface.
8. If necessary continue to etch until all of the oxide is removed.
9. Place sample into the purged transfer box and allow purge for several more minutes.
10. Close and seal transfer box.
11. Transfer sample to the process chamber. Mount samples and pump down

chamber as quickly as possible.

12. Properly dispose of remaining acid solution.

Deposition of Thin Film Solvent

The thin film solvent layers were deposited by either thermal evaporation, ion beam or RF sputtering done at as low a temperature as possible. It was originally thought that all the films could be deposited by evaporation alone, but gallium, indium and tin could not be evaporated successfully. All three materials would deposit on the substrate in small discontinuous droplets. See Figure 2. The coating would appear milky white as opposed to a shinny metallic grey as one would expect. Further examination showed that the sample surface was completely wetted, but that the top surface was extremely bumpy. Additionally, it was observed on subsequent runs that the size of the droplet could be controlled depending on the evaporant melt temperature and therefore the evaporation rate. Unfortunately, they could not be eliminated altogether.

It was thought that the coating was agglomerating on the surface due to oxidation. An attempt was made to reduce the likelihood of oxidation by reducing the evaporation rate, keeping the substrate at as low a temperature as possible, and performing evaporations in a reducing ambient. The film quality improved but not sufficiently to get good results from implantation. Thin coatings of this kind could not successfully be deposited using thermal evaporation. Other solvent materials were tried while simultaneously searching for an outside vendor to lay down an oxide free coating.

Boron oxide was evaporated using a thermal evaporator. Several B_2O_3 coated samples were prepared for ion implantation. Additionally, aluminum was deposited via ion beam sputtering. Indium was successfully deposited using a highly modified, low power, low temperature RF sputter system at Brown University's Thin Film Laboratory. Indium required a capping layer of SiO_2, which was deposited using reactive ion sputtering.

The solvent film thickness was chosen so as to enhance the deposition rate at the substrate-solvent interface. Profile Code[tm] was used to model the implanted carbon distribution. The thickness is chosen such that at the maximum dose and energy the peak of the distribution is two thirds of the depth to the substrate. Also, there should be as little as possible of the tail reaching the substrate. Profile Code's[tm] output is similar to that of Monte Carlo style programs, such as TRIM, but the computation time is much faster, it models multilayer systems, the code includes sputtering effects and it is much more accurate at predicting the important distribution in the tail. An example of a distribution predicted by Profile Code[tm] for carbon into B_2O_3 on silicon is shown in Figure 3.
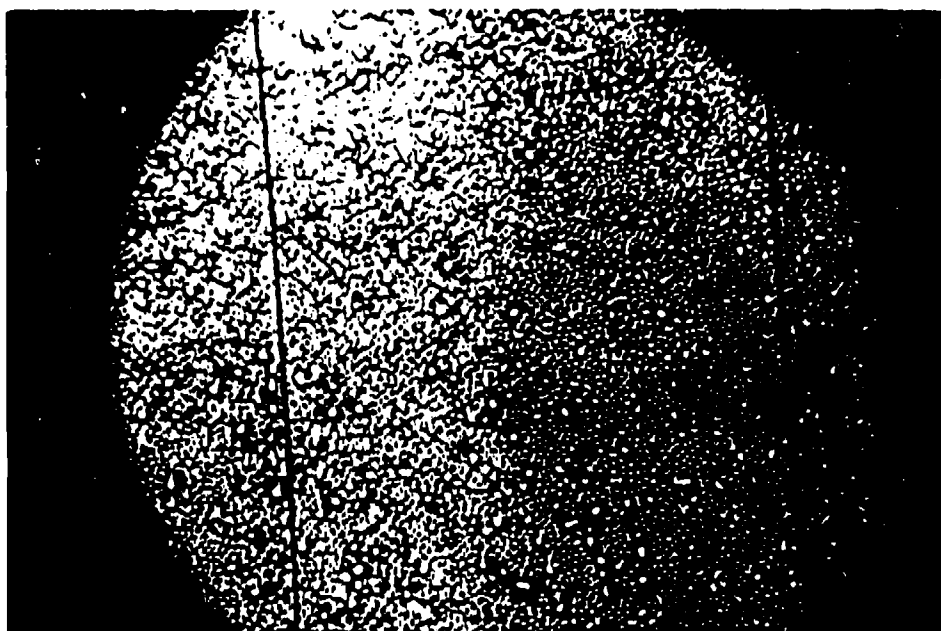
6

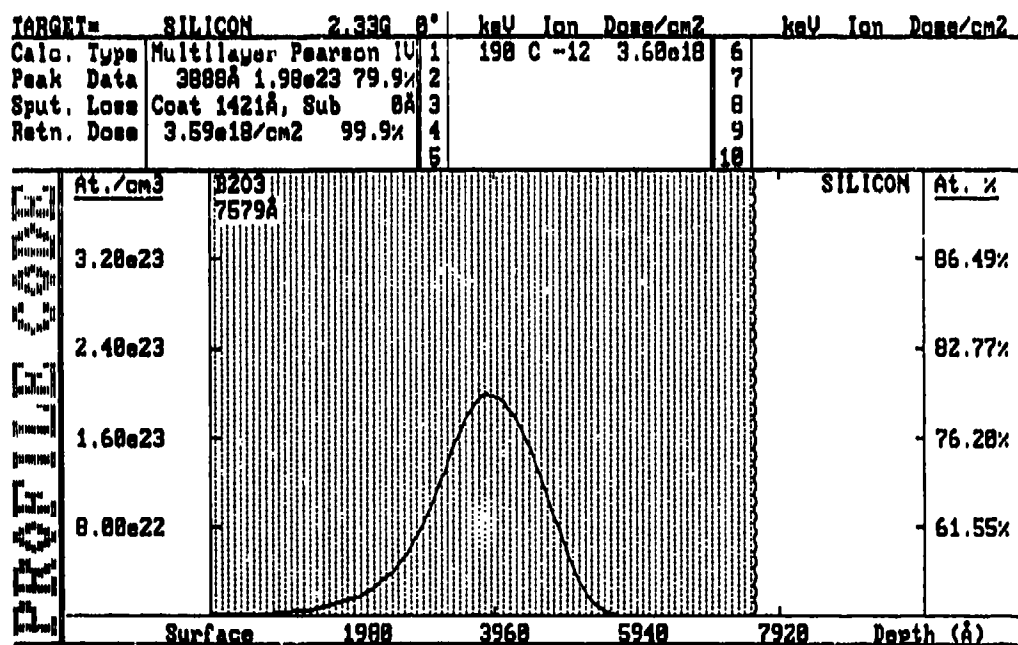Figure 2.Example of Solvent Metal Surface After Thermal Evaporation of Gallium

Figure 3.Profile Code Concentration Prediction for Carbon into B_2O_3

7

2.3   Test Results

Most of the early samples produced were either not ion implanted or emerged from the implantation furnace in a confusing condition. In general, the liquifiable coating appeared to be "balling", resulting in a rough or speckled surface morphology. In some cases it was not clear if one was observing any residual liquid material. If all of the liquid material was lost in the implantation process, then the ions would be directly bombarding the carbonaceous layer, presumably destroying any inherent crystallinity that may have existed in the as-implanted state.

Several liquifiable coatings were tested. These were 1) aluminum, 2) indium, and 3) B_2O_3. Caps of SiO_2 were evaporated on the indium in an effort to retain the material and minimize any balling that may be occurring. B_2O_3 was the first material to actually be exposed to the ion beam. A coating, nominally 1 micrometer in thickness and 5/16 inches in diamter, was deposited on a silicon wafer substrate. This sample was thermally isolated from the cooled substrate in order to allow the carbon beam to provide the necessary heat to liquify the oxide. A thermocouple was used to measure the temperature during the run. Unfortunately, this first run failed when the thermocouple shield melted and damaged the sample.

A second trial was performed using a B_2O_3 sample that was 1.25 micrometers in thickness. The fixture was modified to use a tube furnace to provide heat, rather than relying on the beam heating, and this eliminated the need for a local thermocouple. A narrowly scanned carbon beam at 190 keV was used.   Figure 4 showed a Profile Code prediction of the distribution of carbon atoms in the B_2O_3 for a dose of 3.6×10^{18} atoms/cm^2. This is sample #1 in Table 4. Inspection of the sample after the run showed a highly roughened surface which appeared to consist of deposits of graphite in a matrix of B_2O_3. Further inspection showed that these graphite islands adhere to the substrate, and the substrate tends to be eroded under the boron oxide zones. A test was performed to determine the approximate evaporation rate of boron oxide at the 850°C furnace temperature needed to melt the material, and it was showed that about 1300 Angstroms/hour was being lost. Given the long ion implantation time needed to achieve the large doses required, this rate would result in the loss of most of the B_2O_3 and the subsequent crystal damage of any diamond that may have formed early in the run.

A third trial of boron oxide (sample #2) was performed at a temperature of 600-650°C in an effort to lower the evaporation rate for the 1.1 micrometer thick sample. Measurements indicated that the loss rate was now reasonable. The resultant surface morphology was similar to that of sample #1, carbon islands in a boron oxide matrix. There were also indications that a carbon reaction with the oxygen in the boron oxide may be occurring. In general, the prospects for further study with boron oxide as the solvent did not appear promising, and this material was dropped from further consideration.

Aluminum was the next solvent material to be tested. No cap was needed and the coating was reasonably easy to deposit. Aluminum was not a prime candidate as a solvent because its phase diagram, shown in Figure 4, indicates that chemical reactions with carbon can occur. It was tested because the indium deposition problem had not yet been solved.

8

Table 3. Summary of All Test Samples and Subsequent Analyses

| Sample	Solvent	Substrate	Ion	Dose	Temp.	Tests	
1	B2O3	‹11› Si	C12	3.6e18	900	Etched	Graphite, Si etched, CO reaction
2	B2O3	‹11› Si	C12	1.1e18	500	Graphite, Si etched, CO reaction	X-ray diff., AES, beta SiC
3	Al	‹11› Si	C12	1.8/3.6e18	700	X-ray diff., AES, beta SiC	
4	Al	‹100› diamond	C13	9.1e17	700	not analyzed	
5	Al	6H SiC	C13	.91/1.7e18	700	microprobe, graphite?	
6	3200A In	‹11› Si	C12	2.0e18	500	X-ray, AES, no graphite, SiC?	
7	In	‹11› Si	none	- -	500	Control, form In2O3	
8	3000A In	6H SiC	C13	2e18	400	Graphite, hexagonal substrate	
9	3000A In	‹100› diamond	C13	2e18	400	SIMS, amorphous carbon?	
10	4500A In	‹100› diamond	C13	4e18	450	Raman sees no diamond peak	

9
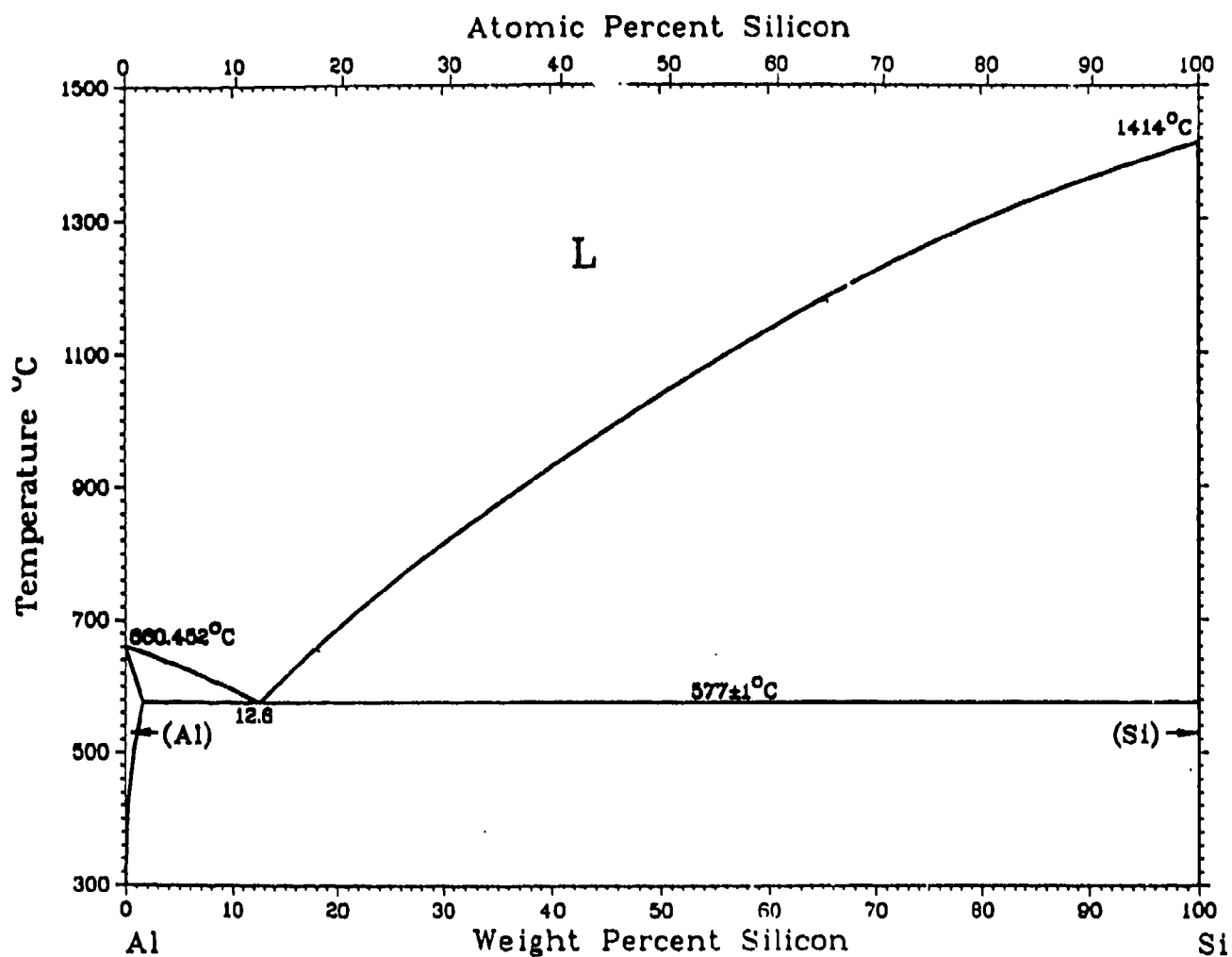
Figure 4.Phase Diagrams for Aluminum - Silicon.

Silicon wafer substrates cut on the <111> axis were used after the usual oxide removal treatment. Also tested were substrates made from silicon carbide and diamond. These are samples #3-#5 in Table 3. Since the latter two substrates already contained carbon, a C^{13+} ion beam was used in order to permit differentiation of the deposit from the base material. A 700°C temperature was used for all the samples to guarantee the melting of the aluminum. Typically, each had nominally 1 micrometer of deposited aluminum. All implants were at 190 keV at the doses indicated in the table, and a tube furnace was used for these and all subsequent implantations.

Sample #3 was tested using x-ray diffraction. Two samples, one receiving a low dose of $1.8 E 18 C^+/cm^2$ and one receiving twice that dose were examined. Figure 5 shows the x-ray diffraction spectrum of the low dose sample. The data definately shows the presence of aluminum and silicon, and a peak of 75° which corresponds to a diamond peak. Figure #6 shows the x-ray diffraction data for the higher dose sample. Interestingly, several broad peaks have increased intensely indicating a deposition in the material. The sharp <111> Si peak has become broadened probably due to ion bombardment and the peak at 75° has grown significantly. Individual peaks have been identified by the computer and marked for identification. Note that in x-ray diffraction, one does not necessarily see all of the peaks indicated in reference spctra, or at exactly the some relative amplitudes. Much depends on the characteristics of the sample, although it is certainly desirable to make an identification with multiple peaks if possible.

Figure 7 shows some relavent comparison spectra. The x-ray data should be capable of excluding some crystalline form as not being present, unless the peaks involved are in interference with some other element's peaks. No indication of carbon in the graphite form was observed. The likelihood of the diamond form also was finally determined to be low. One rather broad, weak peak at 75° was at first thought to suggest that some diamond may have grown on the SiC that appeared with strong peaks, but since only one peak was a candidate and it was somewhat shifted from the expected angle, the chances of having formed any good quality diamond was decided to be low. However, the beta silicon carbide layer appears to have grown well, and very strong peaks are observed.

Sample #3 was also examined with Auger Electron Spectroscopy (AES) to determine the composition with depth in a small region. Figure 8 shows the results of this analysis. The residual aluminum is not very apparent, suggesting that most of it was lost during the implantation. There is virtually no aluminum at the surface, reaching only a modest 20 at.% deep below the surface. Most of the coating material is carbon presumably mixed with SiC. The silicon curve is especially revealing. It shows a nearly constant distribution at the 8% level until the substrate silicon is encountered. This constant value is speculated to be due to the dissolution of the substrate by the molten aluminum. Since the concentration is so constant, it is thought that it could only be resulting from a fixed solubility effect. If this is true, then aluminum is not a desirable solvent, at least when silicon wafers are used as the substrate.
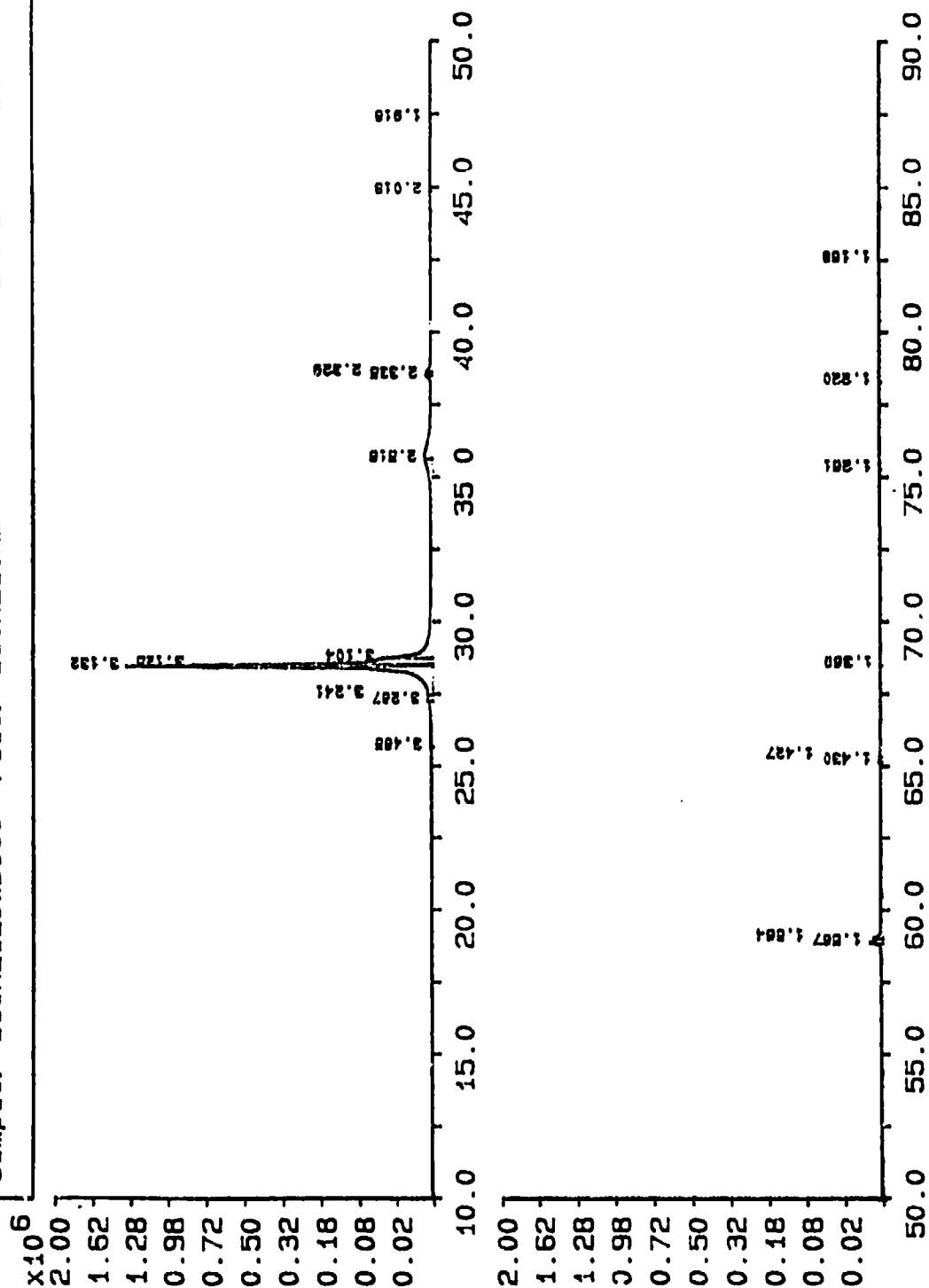
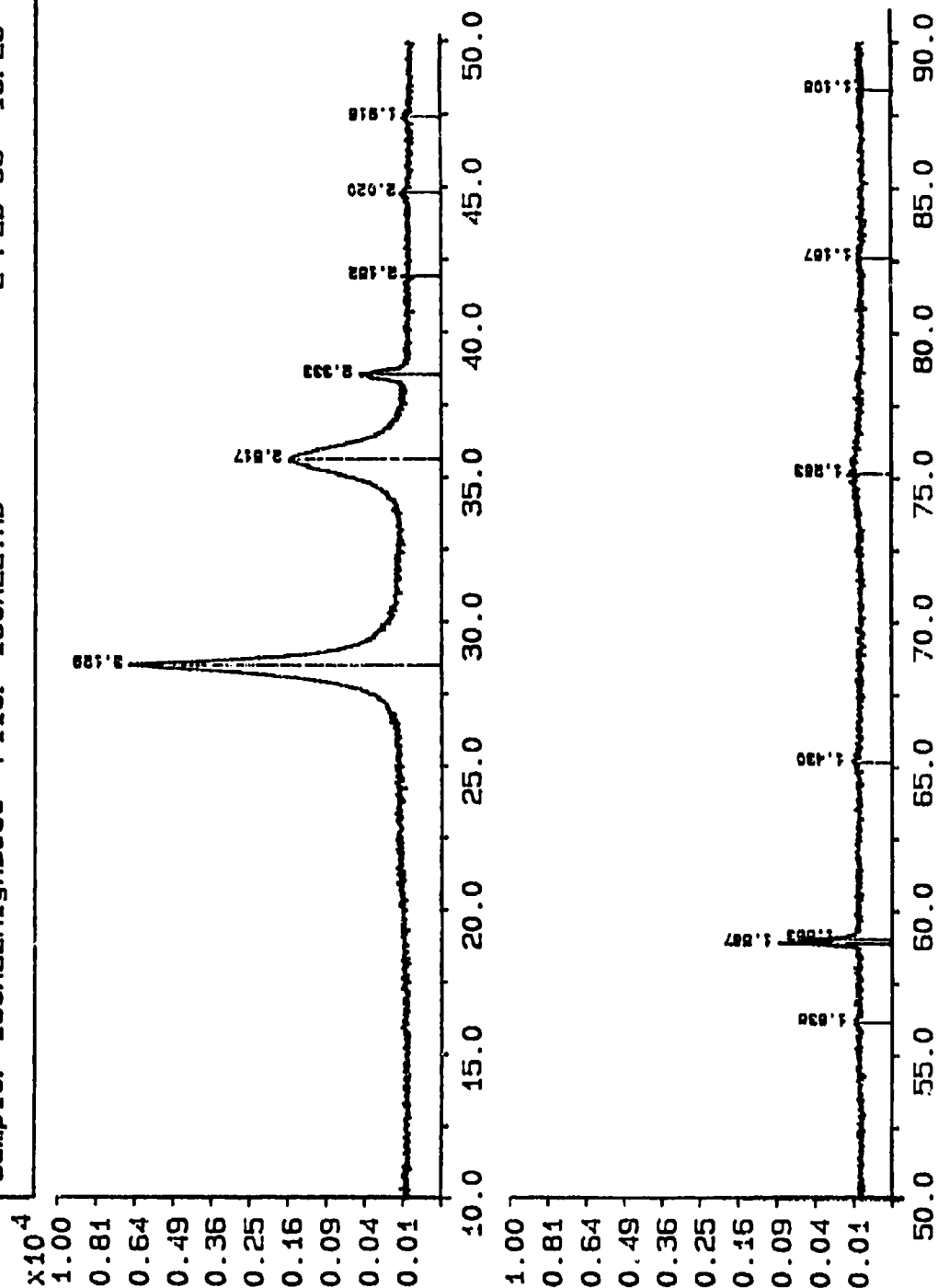Figure 5. X-ray Diffraction Data for Aluminum-on-Silicon, Sample #3. Low Dose.

12

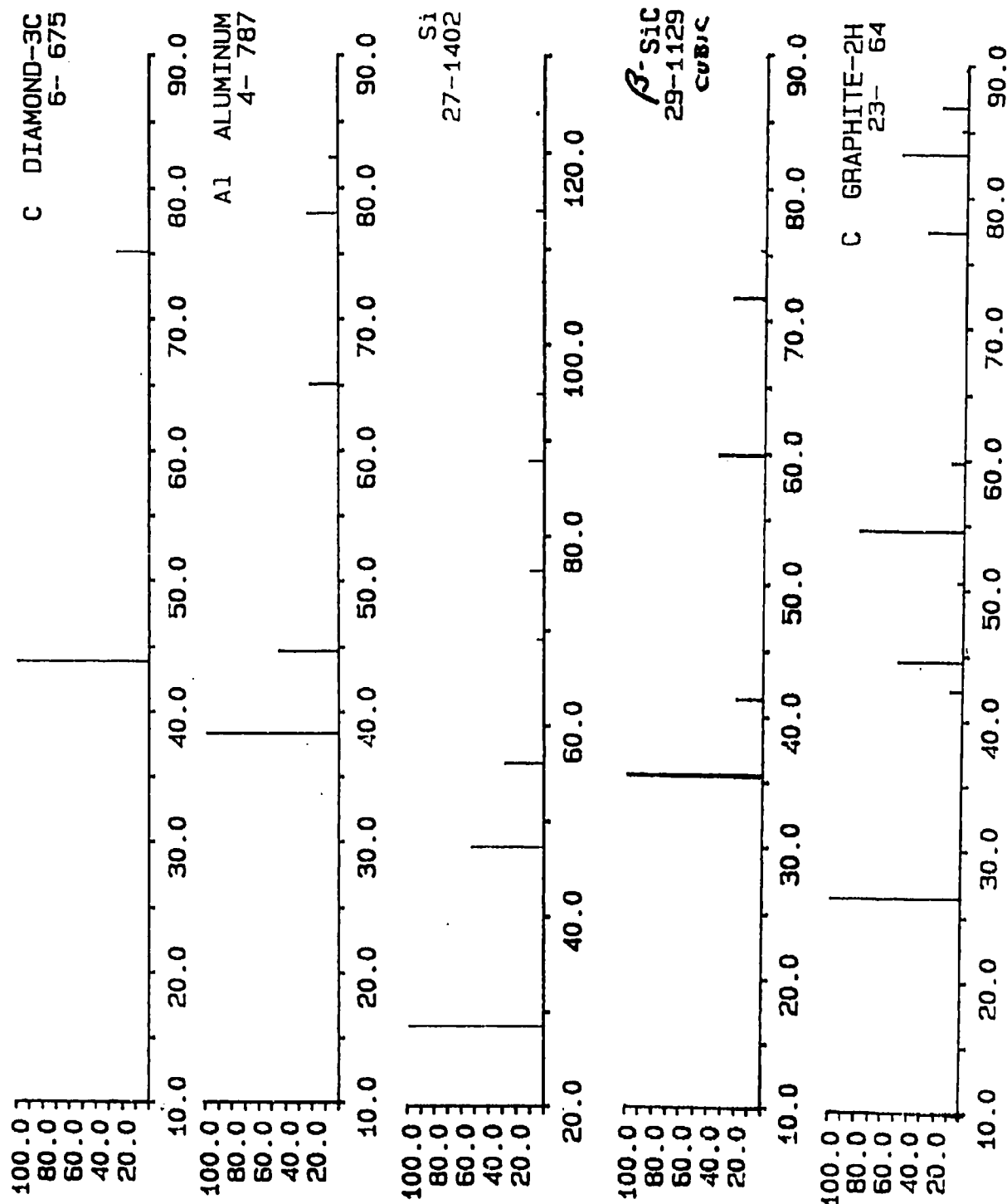Figure 6. X-ray, Diffraction Data for Aluminum-on-Silicon, Sample #3. High Dose.

13

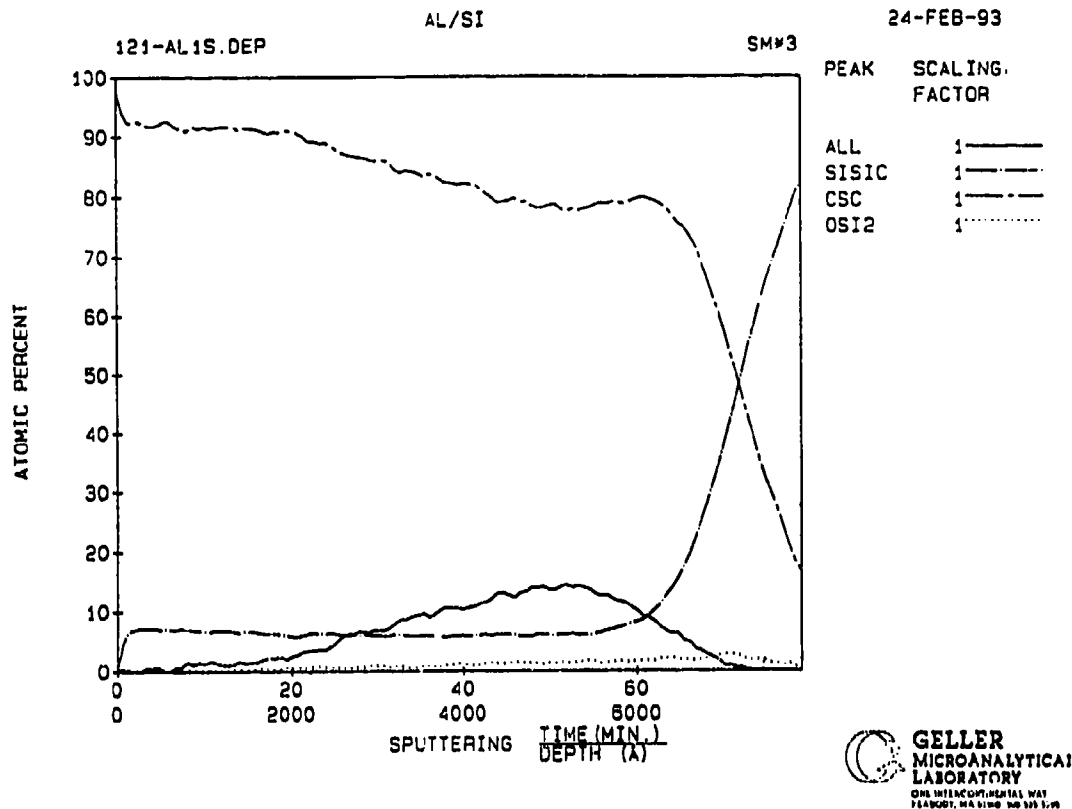Figure 7. Comparison Spectra for X-ray diffraction of Diamond, Aluminum, Silicon, ß Silicon Carbide and Graphite.

14

PEAK	SCALING. FACTOR
ALL	1
SISIC	1
CSC	1
OSI2	1

ATOMIC PERCENT

SPUTTERING TIME (MIN.)
DEPTH (A)

GELLER
MICROANALYTICAL
LABORATORY
ONE INTERCONTINENTAL WAY
PEABODY, MA 01960 508 535 5700

Figure 8. AES Data Showing Composition with Depth for Aluminum-on-Silicon, Sample #3.

Sample #5 was examined with an electron microprobe to determine composition. This substrate was 6H SiC, which implies an hexagonal lattice. As such, one would expect that carbon would be more prone to deposit in the hexagonal graphite form, and this is what is believed to have occurred, based on the appearance of the sample.

Based on these results for aluminum and the identification of a vendor for indium coatings, it was decided to abandon further work with aluminum and emphacize the indium.

Five more samples (#6-#10) were produced using indium as the liquifiable coating. Substrates were silicon, SiC, and diamond. The ions were planned to be C^{13}, which could be distinguished in subsequent tests when the common C^{12} was already in the substrate. The reason for using a diamond substrate was to give the process the best chance of forming a single crystal diamond layer. If it couldn't make diamond on diamond, then the concept would not be worth pursuing.
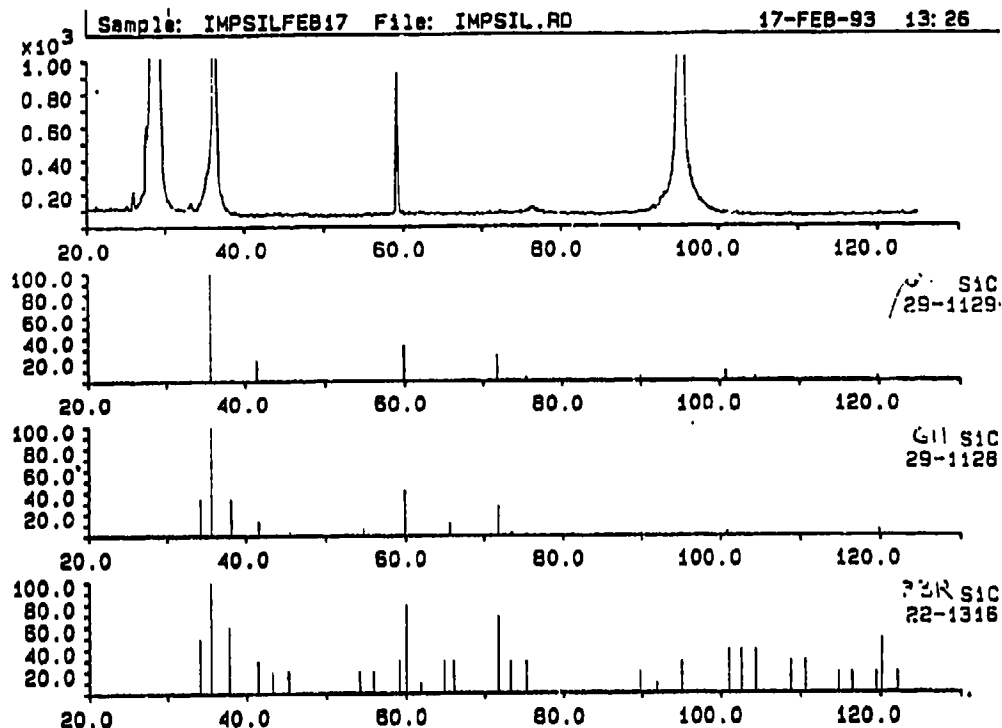
15

Figure 9.X-ray Diffraction Data for Indium-on-Silicon, Sample #6

All indium samples utilized an SiO_2 cap, nominally 1250-1500 Angstroms thick. The implantation parameters are listed in the table. Sample #6 had an x-ray diffraction analysis performed, and the data are shown in Figure 9. Indium tends not to be observed. Once again, there is little evidence of diamond. Prominent diamond peaks are missing and only tiny irregularities in the data exist at the location of minor diamond peaks. The most readily identified peaks appear to be due to silicon, the substrate, and silicon carbide. The exact form of the silicon carbide, beta, 6H, or possibly some other, is not certain from these data since the peaks tend to be little different, as indicated by the comparison spectra in the figure. The large peak at 95° was not identified. Given the substrate, it would appear that the beta form is the most likely to have been produced.

Sample #6 was also checked by AES in correspondence with sample #3, as shown in Figure 10. Indium could not be identified, indicating that it was no longer on the substrate. Here there is no evidence of dissolution of the silicon substrate. The carbon deposit has a variable and small amount of silicon, indicating that the silicon carbide is some sort of mixture in a carbon matrix. Considering that x-ray diffraction did not indicate any crystalline peaks attributable to a form of carbon, one may conclude that the carbon is mostly in an amorphous state.

Sample #8 was indium on 6H SiC. The x-ray diffraction data are shown in Figure 11. A number of peaks are missing, so interpretation is difficult, but it is thought that the <100> peak of graphite at around 42° is visible, as well as a <006> peak at 90°. The <101> peaks
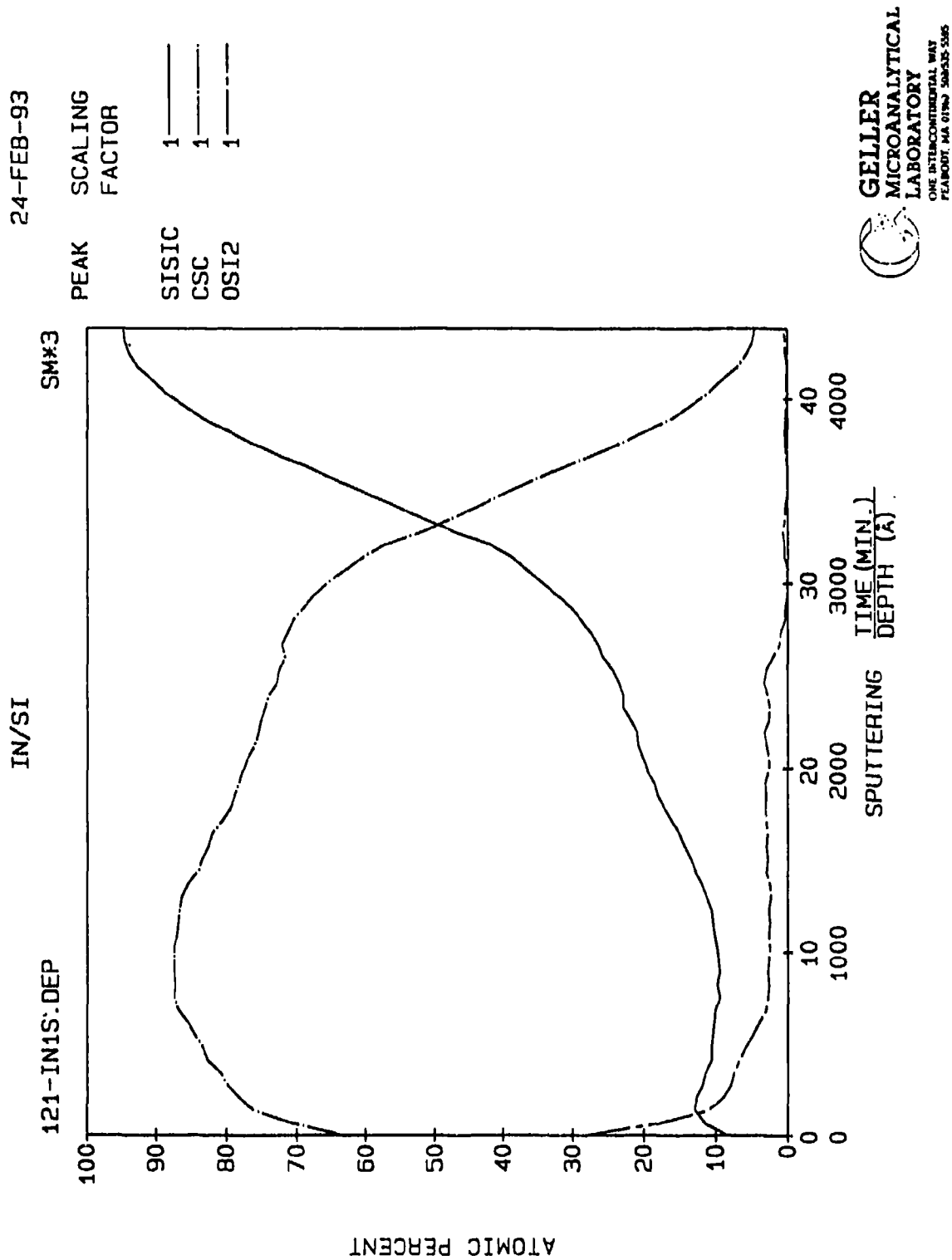
16

Figure 10. AES Data Showing Composition with Depth for Indium-on-Silicon

17
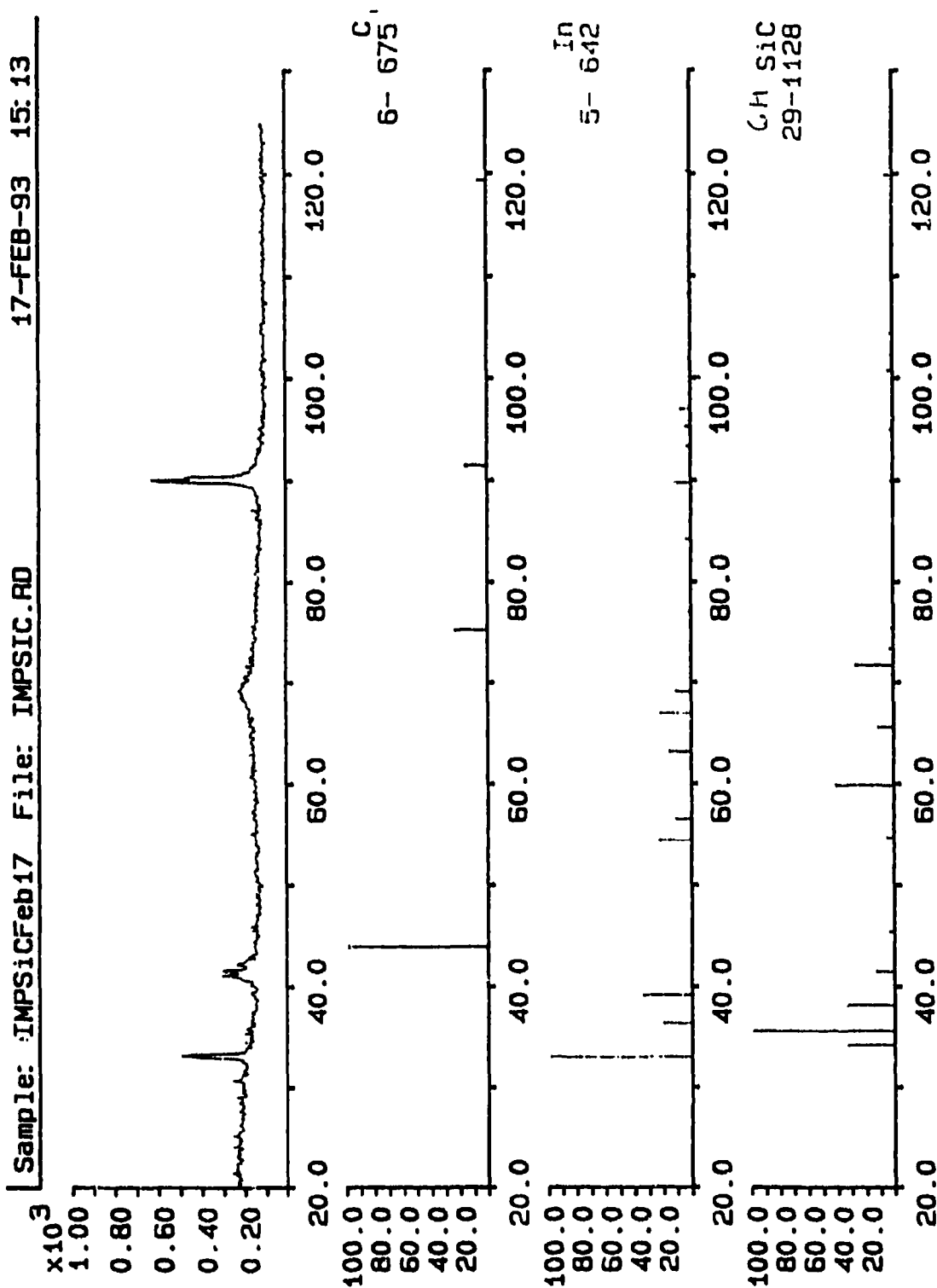
Figure 11. X-ray Diffraction for Indium-on-Silicon Carbide, Sample #8.

18
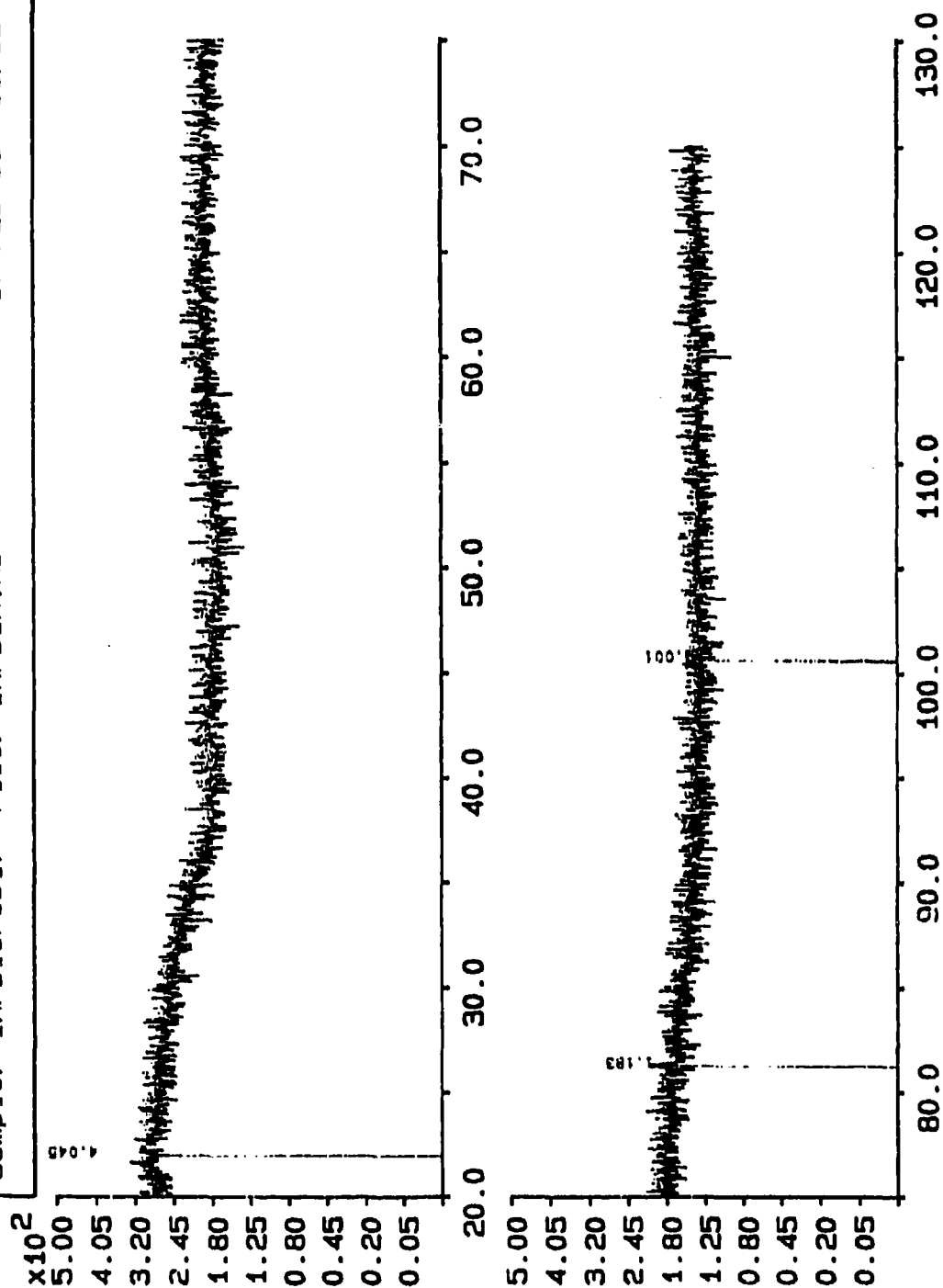
Figure 12. X-ray Diffraction Data for Indium-on-Diamond, Sample #9

19

of indium are thought to be present as well as <202>. Surprisingly, the expected peaks of the substrate 6H SiC are not readily apparent. Thus, it was becoming clear that the x-ray diffraction data could be interpreted in a variety of conflicting ways with samples such as these, and it was uncertain whether any meaningful conclusions could be reach based on these data alone. The x-ray data for sample #9, indium on <100> diamond, emphasizes this conclusion. Figure 11 shows the results plotted to indicate the lattice spacing d. Virtually no peaks are apparent, not even from indium or diamond, and only the computer could pick out the slight variations from noise to "identify" a peak.

Sample #9 was also examined with Secondary Ion Mass Spectroscopy (SIMS), rather than AES. SIMS is more easily capable of differentiating between carbon mass 12 and 13. The data, corrected for SIMS sensitivity and converted to concentrations, are shown in Figure 13. The first dominant characteristic is the lack of solvent, which is many orders of magnitude below the two carbon curves. The second is the high concentration of C^{12} at the surface. Together, these two observations strongly indicate that in this case the solvent was missing very early during the implantation portion of the processing of this sample. Instead, the substrate was simply being ion implanted, resulting in the amorphization or possible graphitization of the diamond substrate and the implantation of C_{13} atoms below the surface.

It was decided to make one last try with a diamond substrate using a thicker indium layer, and this became sample #10. The sample was tested using micro Raman spectroscopy. The surface of the sample is shown in Figure 14, which was covered with yellowish circular areas. The main Raman peak should be shifted for the C^{13} implant compared to the substrate, which is at 1332 for C^{12}. A deposited C_{13} diamond thin film would generate a peak at 1285. Figure 15 is typical of the results obtained. No significant peaks were observed, including that of the substrate. It was concluded that the circular areas were not a crystalline form of carbon and therefore was not evident by Raman spectroscopy. With the failure to identify deposited diamond by even this technique, it was decided to terminate the program.

20
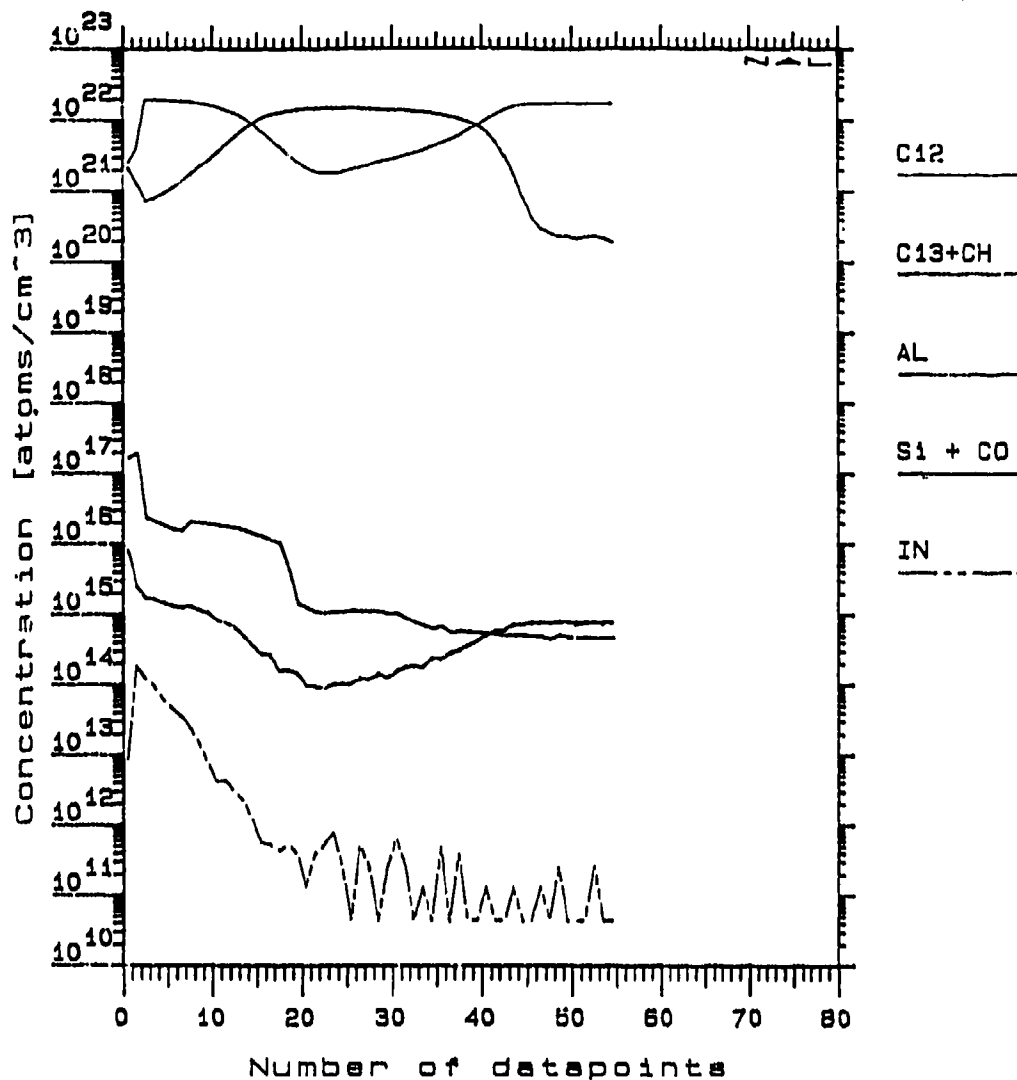
Primary Ions	:	Oxygen	Label	Mass	Cycles	Energy
Ion Energy	:	12 [kev]	C12	12.0	5	0.0
Beam Current	:	300 [nA]	C13+CH	13.0	5	0.0
Scan Width	:	.35 [mm]	AL	27.0	5	0.0
Scan Speed	:	2 [s/Frame]	S1 + CO	28.0	5	0.0
Scan Gate	:	20 [%]	IN	115.0	5	0.0

3538B1 - 3538B5

Normal incidence   Large yellow area

Analytical Answers, Inc.

Figure 13. SIMS Data for Indium-on-Diamond Substrate, Sample #9

21

Figure 14. Sample #10's Surface Covered with Yellow Spots.
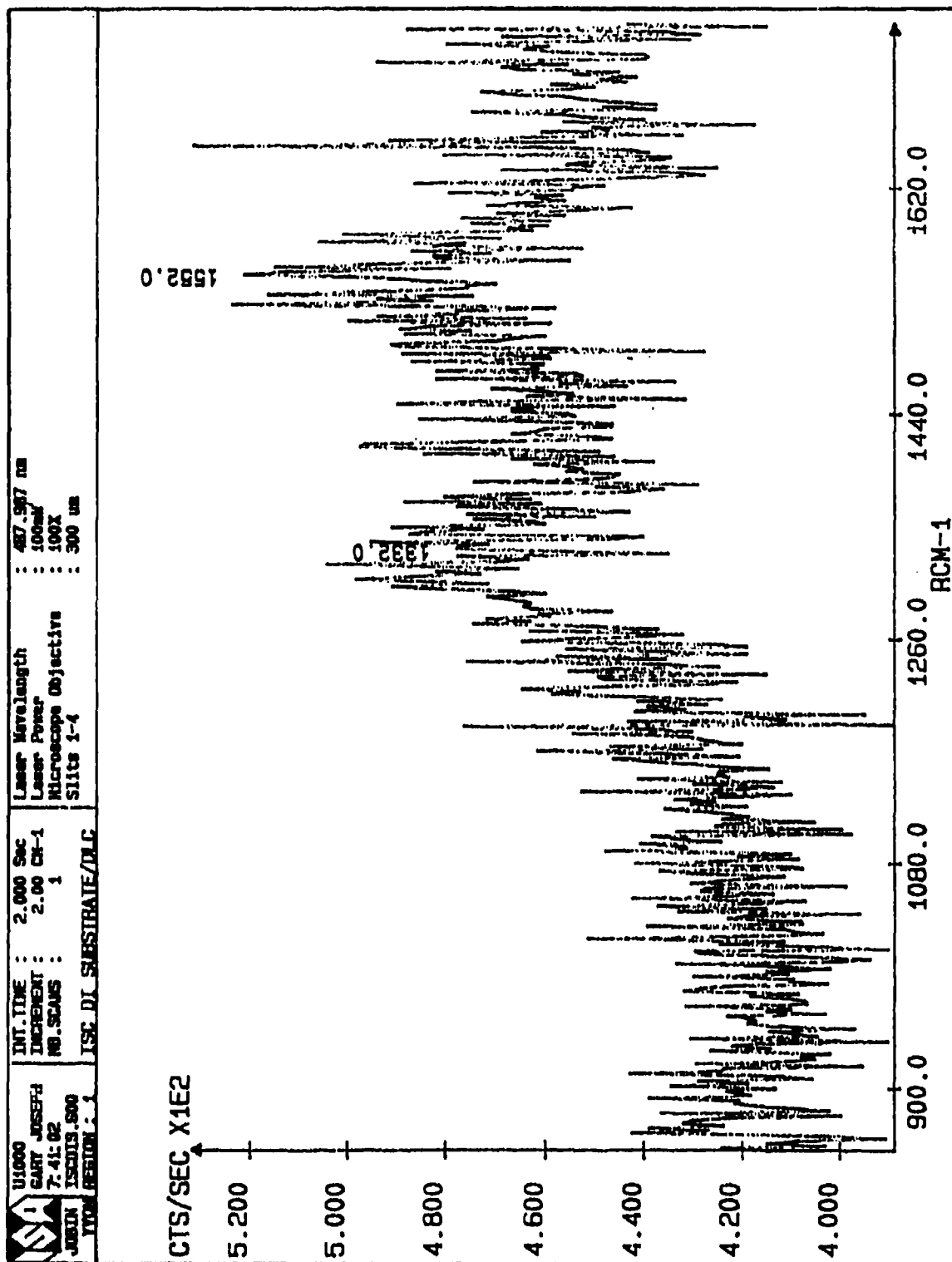
22

Figure 15. Micro Raman Data for Indium-on-Diamond, Sample #1.

23

2.5 Conclusions

The technique of ion implanting into a liquid did not successfully produce a diamond film as desired. Several problems were encountered in applying the technique which had not been anticipated at the beginning of the research. These were:

1.   Deposition and maintenance of oxide-free solvent metal layers
2.   Rapid loss of solvent during ion bombardment
3.   Interaction of solvent with substrate

By the end of the research effort, items 1 and 3 had been solved to what appeared to be a reasonable extent. The loss of solvent was not so easily resolved. All of the AES data and the SIMS data indicated that very little solvent was still present on the surface of the samples, which was not as expected. If the solvent was lost during the implantation, even if a diamond layer had tried to form, the subsequent ion bombardment would have quickly amorphized or graphitized the carbon.

The pattern of circles often seen on the sample surface also suggests that the solvent may have started to form "balls" of material, thus concentrating the remaining carbon in these areas. In areas devoid of solvent, the implantation into the substrate would have reached some equilibrium concentration of carbon with sputtering losses removing any excess over the equilibrium value. In the solvent balls, the carbon could collect to a greater concentration and thickness until the solvent ball itself finally evaporated and/or sputtered away.

Thus, the main technical difficulty seen with the technique is the unexpectedly rapid loss of the solvent material. The rate of sputtering by the beam is predictable, and published data exist on evaporation rates. In the case of aluminum and indium, a measurement of loss rate was made during the program. Nevertheless, even though attempts were made to provide a reasonable margin for the coating thickness, the measurements suggest that the solvent was not present in any significant concentration after the end of the implantation. This discrepancy in the amount of residual solvent has not been resolved despite efforts to vary the temperature, and thus the evaporation rate. At the present time speculations for the loss mechanism include ion beam charging effects and locally high temperatures because of the thermally insulating properties of the substrate and low mass of the solvent coating. This latter argument is not supported by the SIMS data for indium-on-diamond, which suggests that the indium coating was lost very swiftly, while the AES data for indium-on-silicon suggests a slower loss rate. Diamond is a good thermal conductor but a poor electrical conductor.

If further work is performed using this approach, a method will need to be created for maintaining the solvent thickness throughout the bombardment. Such a method might consist

24

of continuously co-evaporating or co-sputtering the solvent during the high temperature phase. Alternatively, the co-deposit might only need to consist of a renewal of the cap material, such as SiO_2, which is much easier to produce in a contaminent-free layer. This more complex system was considered beyond the scope of the present research.

It is not certain whether or not a diamond layer ever formed since the loss of solvent is also consistent with diamond formation followed by subsequent amorphization. More definite is the formation of SiC, which appears in the x-ray diffraction data. The SiC appeared when the substrate was silicon, and based on AES concentration data, it appears that some mixture of C and SiC existed, particularly when aluminum was the solvent. In both cases, the carbon concentration is much greater than that of SiC. Since discreet layers of substrate/SiC/C were not observed, this implies that some silicon must either have dissolved in the solvent metal in both cases in order to bring the silicon out from the substrate, or that the solvent evaporated extremely quickly and most of what is observed is just a very high dose implant of carbon into first silicon and later carbon-in-silicon. The former appears to be more likely in the case of the aluminum solvent because the concentration of the Si is so constant in the carbon layer. The latter model appears to apply to the indium solvent case.

The exact history of the indium-on-silicon sample cannot easily be derived from the AES data. The variable concentration of carbon is not consistent with the hypothesis of "instantaneous" loss of indium solvent. Profile Code calculculations indicate that the carbon depth profile of a 190 keV implant at 2×10^{18} C^+/cm^2 could not reach the concentration level of nearly 90 at.% as measured and that the carbon peak should still be buried several thousand angstroms below the silicon surface. Thus, it must be assumed that the indium solvent survived for perhaps 1/3 to 1/2 of the run and was being lost gradually, rather than in a catastrophic event. As thinning took place, the beam began to first bombard and thicken the initially grown layer of carbon and later passed through that layer and began adding carbon in the silicon substrate beneath. This would account for the "lumpiness" of the AES carbon distribution.

The silicon carbide observed by x-ray diffraction is consistent with growth from dissolved silicon or from carbon implanted into silicon. It has long been known that carbon implanted into silicon makes silicon carbide, and research was previously done at ISC to demonstrate that highly ordered crystalline silicon carbide could be produced if the temperature of the substrate was sufficiently high (>1000°). It is possible that at least some of the material causing the peaks in the x-ray diffraction data has this type of origin.

In conclusion, we find that the straight-forward application of ion implantation into a solvent liquid is significantly more difficult than expected, and some method for maintaining the solvent during the ion bombardment will be needed for any future studies. The results obtained are inconclusive in that it cannot be determined whether or not a diamond film was ever deposited early during the process before solvent loss guaranteed the amorphization of the film.